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(54) Title: MULTI-BLOC COPOLYMER BASED TUNABLE LIGHT EMITTING DIODE, POLYMERS SUITABLE THEREFOR AND OLIGOMERS (57) Abstract <p>The invention is directed to a light emitting diode (LED) emitting light having a wavelength from 400 to 850 comprising an electroluminescing material, electrodes and optionally carrier material and/or reflecting material, said electroluminescing material comprising at least one block copolymer consisting of at least two types of blocks, active blocks sandwiched between non-active blocks, said active blocks being a π-conjugated block of at least 2 and at most 16 monomeric units, said π-conjugated block having a substantially uniform block length throughout the copolymer, and said non-active block having no π-conjugation, optionally with additional electron and/or hole transport properties, to polymers suitable for preparing such LED, to oligomers for preparing said multiblock copolymers and to various processes.</p>		

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Title: Multi-block copolymer based tunable light emitting diode, polymers suitable therefor and oligomers.

The present invention is directed to a tunable light emitting diode (LED) based upon multi-block copolymers, to novel thiophene multi-block copolymers, to thiophene oligomers suitable for preparing said polymers, to processes for preparing said oligomers and said polymers and to the use of said polymers in opto-electronics.

Commercial LED devices are made of inorganic semiconductors e.g. GaAs, GaP etc. which cover almost the whole spectral region. It would be advantageous to have an organic material with electroluminescence in the blue region, as the organic materials are usually more easy to process.

The production of an effective blue LED using organic materials has however not been accomplished yet, which is one of the reasons for the search for alternative materials. Although low molecular weight organic materials are known to give luminescence even with high efficiencies, only recently the use in electroluminescent devices was reported. A disadvantage of the use of low molecular weight organic materials in devices is their tendency to recrystallize.

The use of organic materials in the production of LED has certain advantages, especially from the viewpoint of processability.

One of the important advantages of the polymer LED is its ease of fabrication. The active polymer or prepolymer can be cast from solution on a substrate which makes it possible to fabricate large-area devices. Conjugated polymers can cover the whole spectral region by chemical tuning of the wavelength of the emission by choice of the polymer and control of the conjugation length of the polymer. Another promising feature is the additional use of a conducting

polymer as the hole-injecting electrode resulting in a fully flexible LED.

Suitable candidates for applications in stable optoelectronic devices are conjugated polymers. Polymers can be processed relatively easily and especially large area structures are feasible. The first encouraging results were reported by Burroughes et al (Nature, 347, 477 (1992)), Braun et al. (Appl. Phys. Lett. 58, 1982(1992)) and Grem et al. (Adv. Mater. 4, 36 (1992)), using poly(p-phenylene vinylene)s and poly(p-phenylene) as the electroluminescent layer.

The basic element giving rise to injection luminescence is that of a p-n junction diode operated under forward bias as is illustrated in fig. 1.

The electrons recombine with holes and give rise to bounded excitons, which radiatively decay to photons. In the ideal case each injected electron takes part in the radiative recombination but in practice this is not the case. The quantum efficiency of a device made of an inorganic semiconductor emitting in the visible region lies in the range 0.05 to 4%. The wavelength of the emitted photon is determined by the energy band gap (ideal case). For example GaAs has a band gap of 1.43 eV. In order to obtain visible radiation the energy gap has to be larger than 2 eV. For a blue LED a band gap of 3.4 eV is required. Inorganic semiconductors like SiC with these large band gaps tend to have high resistivities next to fabrication problems because of high melting temperatures and structural stability.

A large number of organic materials have extremely high fluorescent quantum efficiencies in the whole visible spectral region. The major problem with organic crystals is the high voltage needed to inject charges. The drive voltage to obtain a significant light output is in the order of 100 V or above. The use of thin solid films lowers the drive voltage but the efficiency still is extremely low.

Recently it has been reported that LED's can be made of organic thin films by using a multilayer structure. An

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emitting layer is combined with or sandwiched between a hole and an electron injecting layer.

A LED emitting bright blue light was achieved, thus with a luminance of 700 cd/m² at a DC drive voltage of 10 V.

5 Unfortunately the stability of the cell is not good yet. Probably recrystallization of the organic layers due to produced heat causes degradation of the cell.

Burroughes et al. (loc.cit.) and Braun et al. (loc. cit.) clearly demonstrated that LEDs can be made with
10 conjugated polymers. Their main advantage over non-polymeric (in)organic semiconductors is the possibility of processing to form large area structures. The structure of such a LED is shown in figures 2 and 3.

A substrate, usually glass is covered with the
15 transparent electrode, e.g. indium/tin oxide (ITO) functioning as the hole injecting cathode. The emitting layer or a prepolymer is spincoated on top of this layer and covered with a top electrode e.g. Al or Ca, the electron injecting anode. The choice of the electrodes is important. Metals with a low
20 work function give higher efficiencies. Disadvantage of these electrodes is the oxidative instability. By choosing a polymeric substrate polyethyleneterephthalate (PET) covered with transparent processable polyaniline as the hole injecting electrode, G. Gustafsson et al., Nature, 357 477 (1992) even
25 fabricated a fully flexible LED. The electroluminescent polymer used by the above mentioned scientists is poly(p-phenylene vinylene) or a soluble alkoxy derivative thereof.

The electroluminescence spectra of these materials are very similar to their photoluminescence spectra. The
30 photoluminescence of PPV's is assigned to radiative combination of the singlet polaron exciton (also called neutral bipolaron) formed by intrachain excitation.

The electroluminescence is assigned to the same excited state and is generated by recombinations of holes and
35 electrons injected from opposite sides of the structure. The charge carriers are probably polarons. Because the quantum

yield of photoluminescence of PPV is about 4%, the non-radiative processes limit the efficiency of LEDs. This is caused by migration of the excited states to defect sites which act as non-radiative recombination centres. Burn et al. synthesized a copolymer that can be converted by heat treatment from a conjugated/non-conjugated polymer into a fully conjugated polymer. The quantum yields for electroluminescence of the conjugated/nonconjugated polymers were strongly enhanced. The non-conjugate part acting as a trap for the excitons, preventing the migration to quenching sites.

The invention is aimed at providing a light emitting diode (LED) emitting light having a wavelength from 400 to 850 comprising an electroluminescing material, electrodes and optionally carrier material and/or reflecting material, said LED being tunable, stable and easy to manufacture at low cost.

According to the invention said electroluminescing material comprises an electroluminescing material, electrodes and optionally carrier material and/or reflecting material, said electroluminescing material comprising at least one block copolymer consisting of at least two types of blocks, active blocks sandwiched between non-active blocks, said active blocks being a π -conjugated block of at least 2 and at most 16 monomeric units, said π -conjugated block having a substantially uniform blocklength throughout the copolymer, and said non-active block having no π -conjugation.

The invention is based thereon that it has been found to be possible to tune the wavelength of the emitted light by sandwiching π -conjugated blocks having substantially uniform block length between blocks having no π -conjugation, whereby the length of the π -conjugated blocks mainly determines the wavelength of the emitted light. According to the invention this definition of sandwiching π -conjugated blocks between blocks having no π -conjugation is intended to include the situation that both blocks have π -conjugation, whereby there is a large difference in band gaps between the

blocks, resulting therein that there is no π -conjugation between the blocks.

Examples of the components of both the π -conjugated blocks and the σ -conjugated blocks, which may be combined in every possible combination, can be found on the formula sheet (Fig. 4). It is to be noted, that in case the multi-block copolymer is based upon two types of π -conjugated blocks having large difference in band gaps, it is possible to make combinations of two or more of the π -conjugated block materials.

A series of multi-block copolymers with blocks made out of oligothiophenes (π -conjugated) and oligosilane blocks (σ -conjugated) have been tested for the electroluminescence thereof. Data on adsorbance and photoluminescence as a function of conjugation lengths for the oligothiophenes and for oligosilanes respectively, show that with this type of materials the colour of an electroluminescence device can be controlled, not only by adjusting the conjugation length of a π -system, but also by adjusting the conjugation length of a σ -system (polysilanes). Besides, these materials have the advantage that they can be processed with deep UV-photolithography, since the polysilanes are deep-UV photoresists. The stability of the above materials under environmental conditions and under the influence of optical and electric fields used, is comparable to that of PPV, the first polymer material used for electroluminescence device applications.

It is worth noticing that although the mechanical properties of the oligomer blocks are poor, the mechanical properties of the multi-blocks made out of these oligomers generally are excellent and easy to control by adjusting the number of blocks. Further, the solubility as well as some of the electrical and optical properties are controllable by the substituents on the non-active blocks and the π -conjugated blocks. Thus, the above approach gives ample flexibility to tune not only the mechanical, but also the optical and

electrical properties by tuning the length of the oligomers and the number of blocks in the multi-block copolymers and the chemical nature of the side-groups.

Suitable π -conjugated blocks can be based upon all types of components that result in π -conjugation after polymerization to short blocks. Examples thereof are i.a. thiophenes, suitably substituted thiophenes, vinylene, arylene, vinylene-arylene, thiophene-vinylene and thiophene-arylene.

A preferred group of oligomers to be used for the present invention are the, optionally substituted, oligothiophenes.

Other suitable oligomers are based upon the various components given in the formula sheet (Fig. 4).

According to the invention it is essential to use a well-defined π -conjugated block having a substantially uniform block length. This means that all or substantially all π -conjugated blocks in the polymer have the same number of units. In practise this will mean that at least about 90%, preferably at least 98% of the π -conjugated blocks will have the same length. Optionally it is also possible to prepare a block copolymer based upon a mixture two or three different blocks. In that case each of the components will have substantially the same block length.

The π -conjugated blocks can be prepared from the components that give said π -conjugated blocks upon polymerization. Essential is the factor that the block length is substantially uniform. There are various methods in which to obtain said substantially uniform block length. Generally these methods are all based thereon that first an oligomer is obtained having a substantially uniform block length. This can for example be accomplished by oligomerising the monomers in a controlled manner to give rise to a product that is already relatively uniform, optionally followed by purification to obtain the required uniform block length. Another approach is

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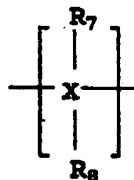
to control the reaction in such way, that the components can only react to give a well-defined product.

An example of this latter approach is to provide a starting material R having two reactive groups, which reactive groups each react with one other reactant, S, to give a product S-R-S that possesses the required block length and π -conjugation (optionally after further treatment, for example removing or adding substituents).

The non-active blocks that can be sandwiched between the π -conjugated blocks can have any composition, provided that they do not provide π -conjugation and that they can be sandwiched between the π -conjugated blocks. Examples thereof are oligo-organo-silanes, substituted silicium blocks and oligo styrene and derivatives thereof.

The choice of the intermediate group has influence on the properties of the multiblock copolymer. Preferred groups are i.a. α , β -unsaturated organic compounds like vinyl and alkylene compounds, oligovinylenes and derivatives thereof, germanium compounds, silicium compounds and carbon compounds.

Suitable materials for said blocks are based on silicium, germanium or on carbon-carbon oligomers. Of the latter group, especially the styrenic materials, like oligostyrene, and oligomers of styrene derivatives, as well as vinyl compounds such as vinylcarbazole are suitable. The silicium, carbon or germanium based materials are preferably of the type.



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wherein X denotes Si, Ge, C, SiO, or CO, R₇ and R₈ being identical or different, each denoting a linear or branched alkyl substituent having 1-6 carbon atoms or a

phenyl, optionally substituted with one or more alkyl and/or alkoxy groups.

The non-active, or σ -conjugated blocks do not have such a strong influence on the wavelength of the LED, although the choice of the blocks and the length thereof certainly influences the behaviour of the LED. Suitable block lengths vary between 2 and 8, said block length being based upon the number of atoms in the σ -conjugated block that become part of the polymer chain.

The silicon-based blocks have the advantage that they can be processed with deep UV-photolithography, since the polysilanes are deep-UV photoresists. The blocks based upon silicium and germanium act also as intrinsic hole transport material, improving thus the quantum efficiency. It is thus possible to prepare a three block copolymer, wherein two types of non- π -conjugated blocks are present, namely one type having hole and another having electron transport properties.

The non- π -conjugated blocks are either directly available chemicals, like vinyl or vinylene oligomers, or can be prepared separately or in situ, i.e. during the assembly of the block copolymer.

According to the present invention new semi-conducting organic and/or organic-inorganic block copolymers can be used, (some of which are shown in figure 4) said polymers being obtainable by making various combinations for the optionally alkylated or alkoxyated active blocks of oligothiophenes, oligovinylenes, oligophenylenes and oligo(p-phenylenevinylene)s (π -conjugated blocks) with oligosilanes (σ -conjugated blocks), oligosiloxanes, oligovinylpyridine, oligostyrene non-active blocks in order to obtain a heterostructure based on the principal of the selfassembly of the block copolymers.

The active block will be sandwiched between the non-active blocks $[(-A_x-B_y-)]_z$, wherein A_x and B_y respectively denote the π -conjugated and the non π -conjugated blocks, x and y being the respective block-lengths and z being the number of $-A_x-B_y-$ blocks in the polymer. The values of x, y and z are

preferably such that the molecular weight of the polymer will be between 2500 and 500,000. Lower values may lead to problems in the processing to films, whereas higher values do not provide additional advantages in terms of polymer properties and may lead to processing difficulties, due to the high molecular weight.

The proposed block copolymers provide various chemical and physicochemical tuning capabilities and improve the properties that have been described previously, concerning the tunable LEDs. Depending on the length of the π -conjugated-blocks and the non-active blocks the wave length of the emitted light is tuned to a value between 400 and 850. The block length, preferably varies between 2 and 16 units, each unit comprising two double and two single C-C bonds. With shorter block lengths the emitted light is more in the blue/green area, whereas larger block lengths lead to a more reddish colour.

Further the ability of the block copolymers to self assemble, thus producing microphase separated ordered structures at the supramolecular level, gives the opportunity to obtain new device architectures or even new devices.

Recently P.L. Burn et al. (Nature, 356, 47 (1992)) have reported an increase in the efficiency of the LEDs by the use of copolymers of conjugated/non-conjugated blocks (PPV-precursors). The synthesis of the copolymers was accomplished by the use of two different leaving groups (methoxy, sulphonium) into a precursor copolymer, from which they can eliminate selectively one of these, or both, to give a fully conjugated copolymer of poly(p-phenylenevinylene) (PPV). A severe disadvantage of the system of Burn et al lies therein that their system cannot provide a well-defined block-length, and thus no well-defined tunable wave length of the LED due to the random character of the elimination reaction.

The σ -conjugated blocks are either directly available chemicals, like vinyl or vinylene oligomers, or can

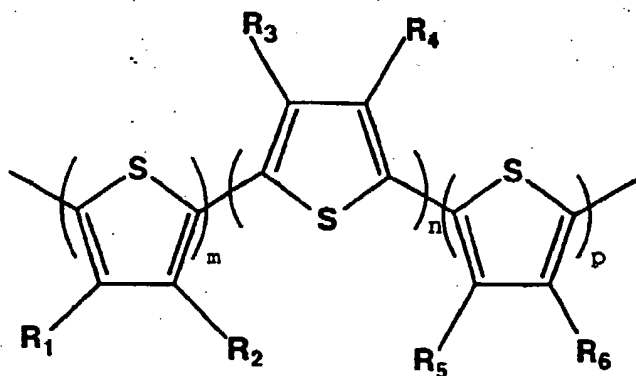
be prepared separately or in situ, i.e. during the assembly of the block copolymer.

The blocks can be assembled into one polymer by known techniques, for example by reaction between the blocks, either directly into one copolymer or in two or more steps.

One of the further objects of the present invention is to provide a novel class of multiblock copolymers containing short blocks of thiophene and derivatives thereof, which multiblock copolymers are suitable for use in optoelectronics and more in particular in LED's, as described herein.

A further object is to provide a novel class of multiblock copolymers containing short blocks of thiophene and derivatives thereof, which multiblock copolymers are easy to process, for example by spin coating, into a thin layer on a substrate.

This block copolymer consists of at least two groups of blocks, thiophene blocks A, sandwiched between non-thiophene blocks B, said thiophene blocks A having the formula 1,



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wherein m, n and p are integers having a value of 0-9, the sum of m, n and p being at least 3 and wherein at least one of R₁-R₆ is different from H. This means that at least one of the rings in each block has at least one R different from H.

The substituent R_1 - R_6 may each be selected from H, optionally branched, lower alkyl, i.e. C_1 - C_{15} and optionally branched, lower alkoxy.

It is to be noted, that the substituents R_1 - R_6 in the blocks may vary within each block.

The block A, the thiophene block, will be sandwiched between the non-thiophene blocks in the manner $[(-A_x-B_y)]_z$, wherein A_x and B_y respectively denote the π -conjugated and the non π -conjugated blocks, x and y being the respective block-lengths and z being the number of $-A_x-B_y-$ blocks in the polymer. The values of x, y and z are preferably such that the molecular weight of the polymer will be between 2500 and 500,000. Lower value may lead to problems in the processing to films, whereas higher values do not provide additional advantages in terms of polymer properties and may lead to processing difficulties, due to the high molecular weight.

Depending on the required properties the number of thiophene units can be selected, as well as the type and number of substituents. It is preferred that at least one of the thiophene rings has to be substituted as otherwise the processability, especially in spin-coating, is insufficient. Preferably at least two of the rings in each block are substituted with alkyl, aryl, alkaryl, aralkyl, alkoxy, aralkoxy and the like, each substituent containing one to 15 carbon atoms. In practising the invention the substituents R_1 and R_2 will generally be identical to R_5 and R_6 , whereas R_3 and R_4 may be different. Preferably the number of substituents on each ring will not exceed one, that means that in each ring at least one of the R-groups will denote H. The selection of the substituents influences the electroluminescent properties of the material to some degree. For the processing properties of the materials the presence of substituents, like butyl, octyl and dodecyl, is very important.

Suitable multiblock copolymers preferably contain 2 to 16 or more thiophene units in each thiophene block.

It is to be noted that when using these multiblock copolymers of the present invention in opto-electronics and more in particular in electro-luminescent devices, the length of the blocks has a profound influence on the wave length of the light. Also important is the choice of the various substituents.

Suitable multiblock copolymers preferably contain 5 or more thiophene units.

The choice of the intermediate group, group B, has also influence on the properties of the multiblock copolymer. In case of use in optoelectronics preferred groups are i.a. α , β -unsaturated organic compounds like styrene and derivatives thereof, germanium compounds and silicium compounds.

Suitable materials for said blocks are those described hereinbefore in relation to the LED.

The blocks can be assembled into one polymer by known techniques, for example by reaction between the blocks, either directly into one copolymer or in two or more steps.

According to the invention new LED's are provided based upon novel semi-conducting organic and/or organic-inorganic block copolymers, said polymers being obtainable by making various combinations of π -conjugated and non- π -conjugated blocks in order to obtain a heterostructure based on the principal of the selfassembling of the block copolymers.

The materials for the electrodes needed for the LEDs and quantum-well devices are chosen appropriately following the work function of the active multi-block copolymers. These materials are well-known in the art of LED's. Suitable materials are described in the literature and can be selected by a person skilled in the art based upon the actual configuration to be used.

Generally the LED comprises two layers of electrodes, such as indium-tin oxide and a conducting metal, between which layers the electroluminescent material has been

sandwiched. The electroluminescent material is preferably spun-coated on the surface of an electrode. In case a flexible LED is required a thin layer of polymer forming a hole injecting electrode, transparent in the region of emission, may be applied to a flexible substrate, for example a polyester. This two layer material forms the cathode of the LED, which is placed in contact with the electroluminescent material. The anode can advantageously be evaporated at low pressure onto the surface of the electroluminescent material. Suitable metals are calcium, indium, aluminium, tin, magnesium and alloys of those materials.

In the figures some aspects of the invention have been elucidated.

In figure 1 the basic element giving rise to injection luminescence, a p-n junction diode operated under forward bias, is illustrated.

In figures 2 and 3 the schematic set-up of an LED is shown and in figure 4 the general structure of some the multi-block copolymers is given.

Figure 5 gives the spectroscopic characterization of thin films of multiblock copolymers with varying block length.

Figures 6-9 give some of the reactions that may be used to prepare the block copolymers used in the invention.

Finally Figure 10 shows the wave length pattern of the electroluminescence of two different multiblock copolymers.

The present invention is elucidated on the basis of the following examples and reaction schemes, without being limited thereto.

General Structure of Poly[(Silanylene)Thiophene]s

Route A. Polycondensation of dilithiumsalt of oligothiénylene and oligosilanylene. (fig 9)

Route B. Cross coupling of digrignard-bisthiénylsilanylene and dibromooligothiénylene. (fig 9)

$R_1, R_2, R_3, R_4, R_5, R_6 = H, C_1-C_{20}$ linear or branched alkyl or alkoxyalkyl; $R_7, R_8 = C_1-C_{20}$ linear or branched alkyl, aryl; $n = 0-3$; $m = 0-4$; $q = 1-8$.

5 Example 1

Synthesis of poly[(dibutylsilanylene)terthiophene].

10 Dibutyldichlorosilane (5 mmol) in 10 ml of diethylether was added to the dilithiumsalt of 2,2':5',5"-terthiophene (5 mmol) in 25 ml of dimethoxyethane. Refluxing for 1 hour and precipitation from chloroform in cold methanol, acetone and methanol again, gave pure pale yellow product (50%).

15

Example 2

Synthesis of (T6Oct2Si2Me4)_n.

20 Two equivalents n-BuLi were added to 1.41 g (5 mmol) of bisthienyltetramethyldisilane dissolved in 50 ml THF. By adding two equivalents of MgBr₂·Et₂O in Et₂O the dilithiumsalt was converted to the diGrignard. Subsequent addition of an equimolar amount of dibromodioctyltetrathienylene and 1%
25 NiCl₂·dppp afforded a dark red solution which was stirred overnight. The crude reaction mixture was precipitated in excess methanol. The precipitate, a dark red solid, was vacuum dried yielding 3.46 g (83%) polymer.

30 Synthesis of 3,3"-di-n-octyltetrathienylene.

 2-Iodo-3-octylthiophene (112.8 g, 0.35 mol) in 250 ml of diethylether was slowly added to 0.70 mol of magnesium turnings in 50 ml of diethylether (1 hour). This mixture was
35 refluxed for 2 hours. The Grignard was decanted and added to 0.14 mol of dibromobithienyl (45.4 g, 0.14 mol) and 1.5 g of

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NiCl₂.dppp in 200 ml of diethylether. The mixture was stirred overnight, poured into 1000 ml of a cold 5% aqueous NH₄Cl solution. The aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with water and brine and dried over MgSO₄. Removal of the solvent afforded a brown viscous oil, that was purified by flash chromatography (aluminiumoxide / pentane). Repeated crystallization from acetone (50 ml) yielded 50.5 g (66%) of a yellow solid.

10 Synthesis of 5,5''-dibromo-3,3''-di-n-octyltetrathienyl.

3,3''-di-n-octyltetrathiophene (20 g, 36 mmol) was dissolved in acetic acid/chloroform (150 ml). To this mixture NBS (12.8 g, 72 mmol) was added. The mixture was stirred for 15 1.5 hours at 45 °C. After addition of chloroform (200 ml), the mixture was neutralized with a KOH solution. The organic layer was washed with water and brine and dried over MgSO₄. After removal of the solvent, the crude product was crystallized from CH₂Cl₂ / acetone (2/1). Yielding 20.2 g (79%) of pure 20 brown-yellow product.

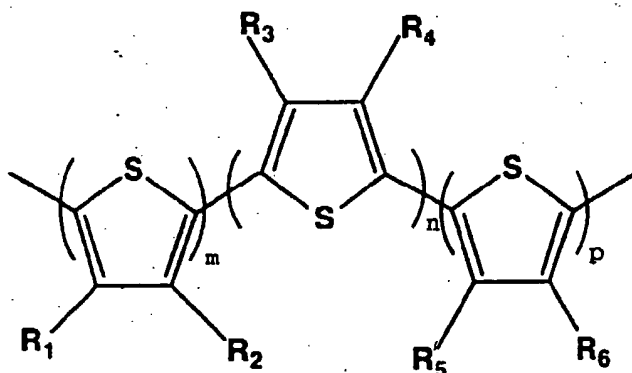
Preparation of films

Thin films of the polymers were prepared by spincoating 25 5-15% solutions of the various polymers in an organic solvent on a glass slide covered with Indium Tin Oxide (ITO). Various metal electrodes (Ca,Al,In,Sn,Mg and alloys of these metals) were evaporated at low pressure (10⁻⁶ torr). The films were assembled into an LED. The wave length pattern of the 30 electroluminescence of two different multiblock copolymers has been given in Fig. 10.

CLAIMS

1. Light emitting diode (LED) emitting light having a wavelength from 400 to 850 nm comprising a layer of an electroluminescing material, electrodes and optionally carrier material and/or reflecting material, said electroluminescing material comprising at least one block copolymer consisting of at least two types of blocks, active blocks sandwiched between non-active blocks, said active blocks being a π -conjugated block of at least 2 and at most 16 monomeric units, said π -conjugated block having a substantially uniform block length throughout the copolymer, and said non-active block having no π -conjugation.
2. LED according to claim 1, wherein the monomeric units of the π -conjugated block have been selected from the group consisting of thiophene, alkylated, alkoxyated and arylated thiophene, vinylene, optionally substituted phenylene, optionally substituted p-phenylene-vinylene, vinylene-thiophene, alkylated, alkoxyated and arylated vinylene-thiophene, and combinations of two or more of these monomeric units.
3. LED according to claim 2, wherein the monomeric units of the π -conjugated block have been selected from the group consisting of substituted and unsubstituted thiophene, alkylated, alkoxyated and arylated thiophene.
4. LED according to any one of the claims 1-3, wherein the non-active, non- π -conjugated block has been selected from the group consisting of α , β -unsaturated organic compounds like vinyl and alkylene compounds, oligovinylenes and derivatives thereof, germanium compounds, silicium compounds and carbon compounds.
5. LED according to any one of the claims 1-4, wherein the at least one block copolymer comprises as at least one third block a hole or electron transport controlling block.

6. LED according to any one of the claims 1-5, wherein an additional layer is present having hole and/or electron transport controlling properties.
7. LED according to claim 6, wherein the material of the said additional layer is polysilane.
8. LED according to any one of the claims 1-7, wherein the said electroluminescing material is used in admixture with a material influencing the hole transport properties, for example a polysilane.
9. LED according to any one of the claims 1-8, wherein a thin layer of polymer forming a hole injecting electrode, transparent in the region of emission, is applied to a flexible substrate, for example a polyester.
10. Block copolymer consisting of at least two groups of blocks, thiophene blocks A sandwiched between non-thiophene blocks B, of the formula $[(-A_x-B_y-)]_z$, wherein A_x and B_y respectively denote the thiophene and the non-thiophene blocks, x and y being the respective block-lengths and z being the number of $-A_x-B_y-$ blocks in the polymer, said thiophene blocks A_x having the formula 1,



1

- wherein m, n and p are integers having a value of 0-9, the sum of m, n and p being at least 4 and wherein at least one of R_1-R_6 is different from H.

11. Block copolymer according to claim 10, wherein the substituents R_1-R_6 are selected from H and alkyl, aryl, alkaryl, aralkyl, alkoxy, aralkoxy, preferably from H,

optionally branched, lower alkyl, i.e. C₁-C₁₅ and optionally branched, lower alkoxy.

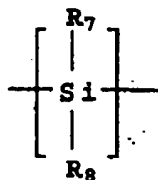
12. Block copolymer according to claim 10 or 11, wherein the values of x, y and z are such that the molecular weight of the polymer will be between 2500 and 500,000.

13. Block copolymer according to claim 10-12, wherein at least two of the rings in each block are substituted with alkyl, aryl, alkaryl, aralkyl, alkoxy, aralkoxy and the like, each substituent containing one to 15 carbon atoms.

14. Block copolymer according to claim 10-13, wherein the number of substituents on each thiophene ring does not exceed one.

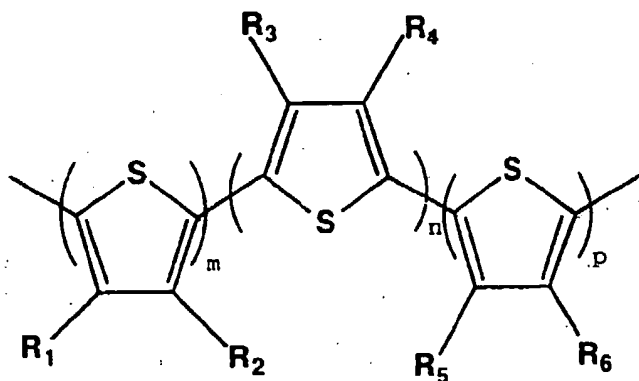
15. Block copolymer according to claim 10-14, wherein the group B is selected from the group consisting of α , β -unsaturated organic compounds like styrene and derivatives thereof, germanium compounds and silicon compounds.

16. Block copolymer according to claim 15, wherein the group B is



R₇ and R₈ being identical or different, each denoting a linear or branched alkyl radical having 1-6 carbon atoms or a phenyl radical, optionally substituted with one or more alkyl and/or alkoxy groups.

17. Thiophene oligomer, suitable for preparing a multiblock copolymer according to claim 10, wherein said thiophene oligomer has the formula 1,



1

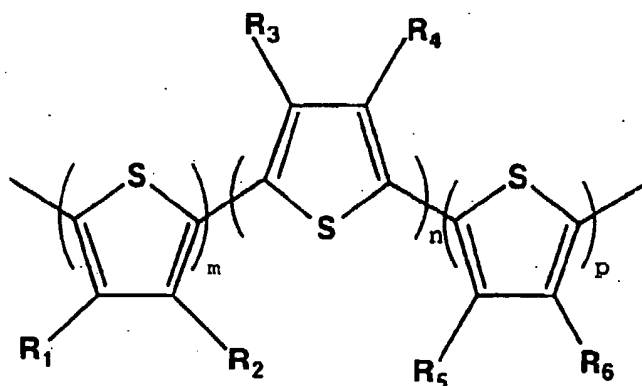
wherein m, n and p are integers having a value of 0-9, the sum of m, n and p being at least 4 and wherein at least one of
 5 R₁-R₆ is different from H.

18. Thiophene oligomer according to claim 17, wherein the substituents R₁-R₆ are selected from H and alkyl, aryl, alkaryl, aralkyl, alkoxy, aralkoxy, preferably from H, optionally branched, lower alkyl, i.e. C₁-C₁₅ and optionally
 10 branched, lower alkoxy.

19. Thiophene oligomer according to claim 17 or 18, wherein at least two of the rings in each block are substituted with alkyl, aryl, alkaryl, aralkyl, alkoxy, aralkoxy and the like, each substituent containing one to 15
 15 carbon atoms.

20. Thiophene oligomer according to claim 17-19, wherein the number of substituents on each thiophene ring does not exceed one.

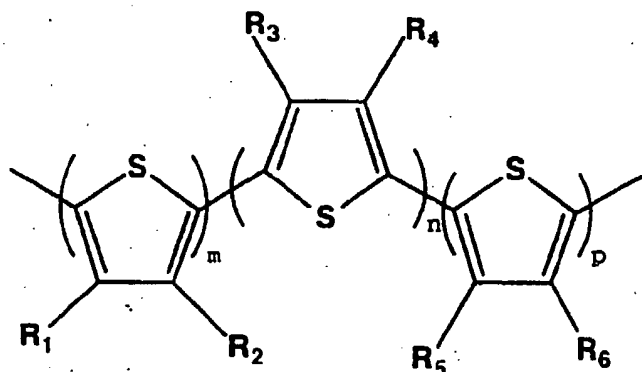
21. Process for preparing a block copolymer consisting
 20 of at least two groups of blocks, thiophene blocks A sandwiched between non-thiophene blocks B, of the formula $[(-A_x-B_y-)]_z$, wherein A_x and B_y respectively denote the thiophene and the non-thiophene blocks, x and y being the respective block-lengths and z being the number of -A_x-B_y-
 25 blocks in the polymer, said thiophene blocks A_x having the formula 1,



1

wherein m, n and p are integers having a value of 0-9, the sum of m, n and p being at least 4 and wherein at least one of R₁-R₆ is different from H, substantially as described herein.

22. Process for preparing a thiophene oligomer, wherein an oligomer is prepared having the formula 1,



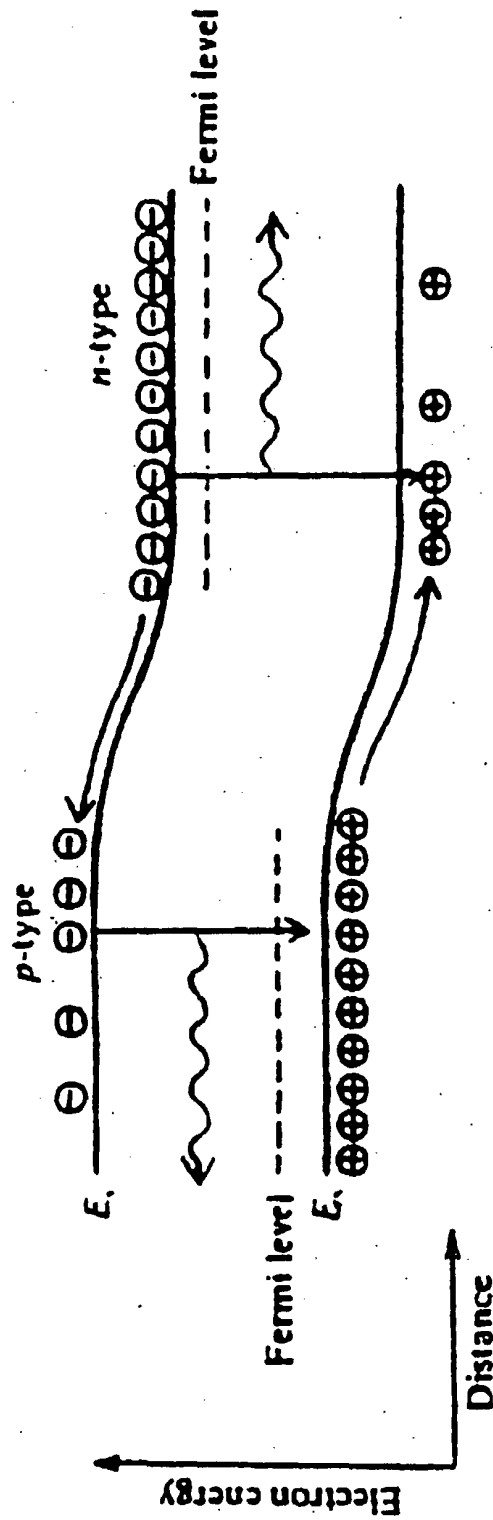
1

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wherein m, n and p are integers having a value of 0-9, the sum of m, n and p being at least 4 and wherein at least one of R₁-R₆ is different from H, substantially as described herein.

23. Use of the multiblock copolymers according to anyone of the claims 10-16 in optoelectronics.

24. Film, optionally on a substrate, of a multiblock copolymer according to any one of the claims 10-16.



Injection of minority carriers and subsequent radiative recombination with the majority carriers in a forward biased p-n junction.

FIG.1

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Light Emitting Diodes

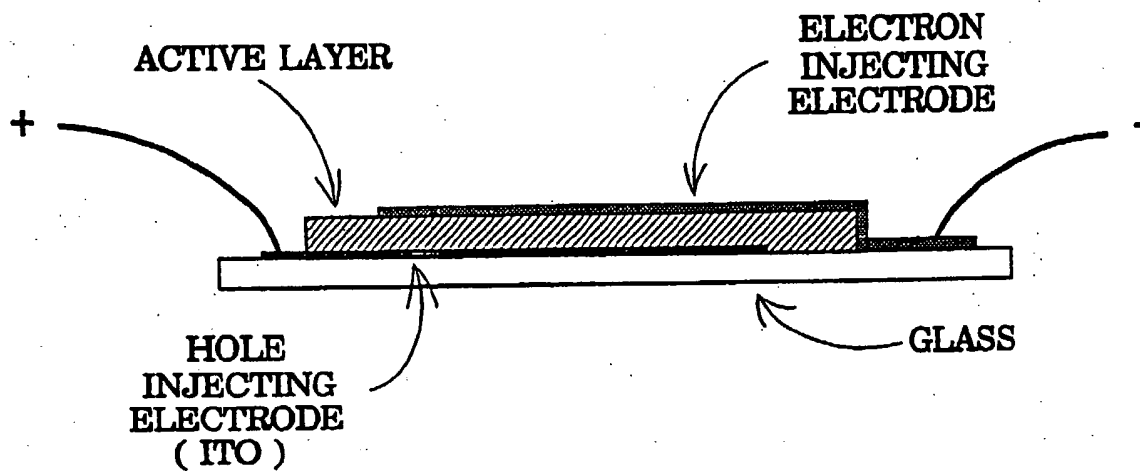


FIG. 2

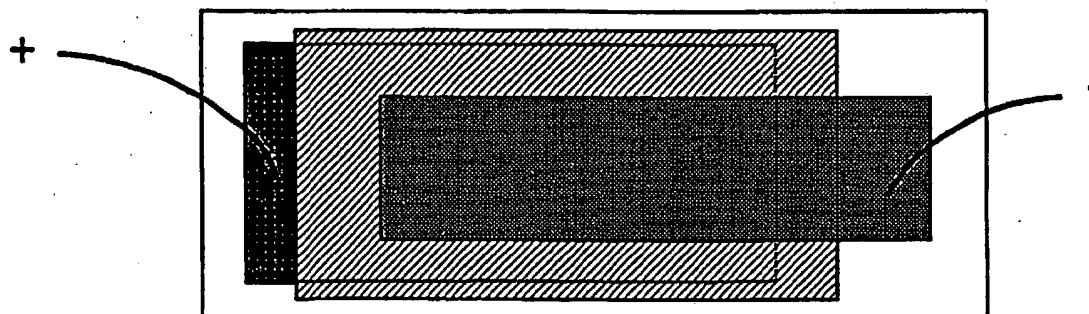
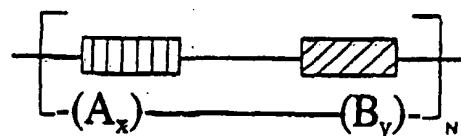
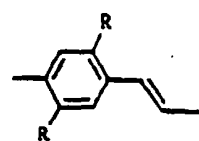
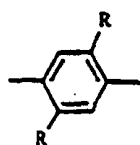
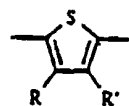


FIG. 3

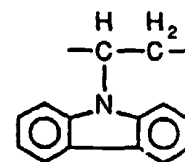
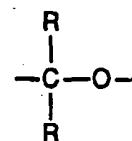
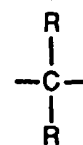
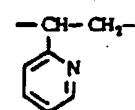
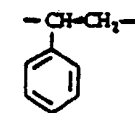
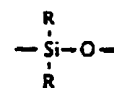


A_x
($x=1-16$)



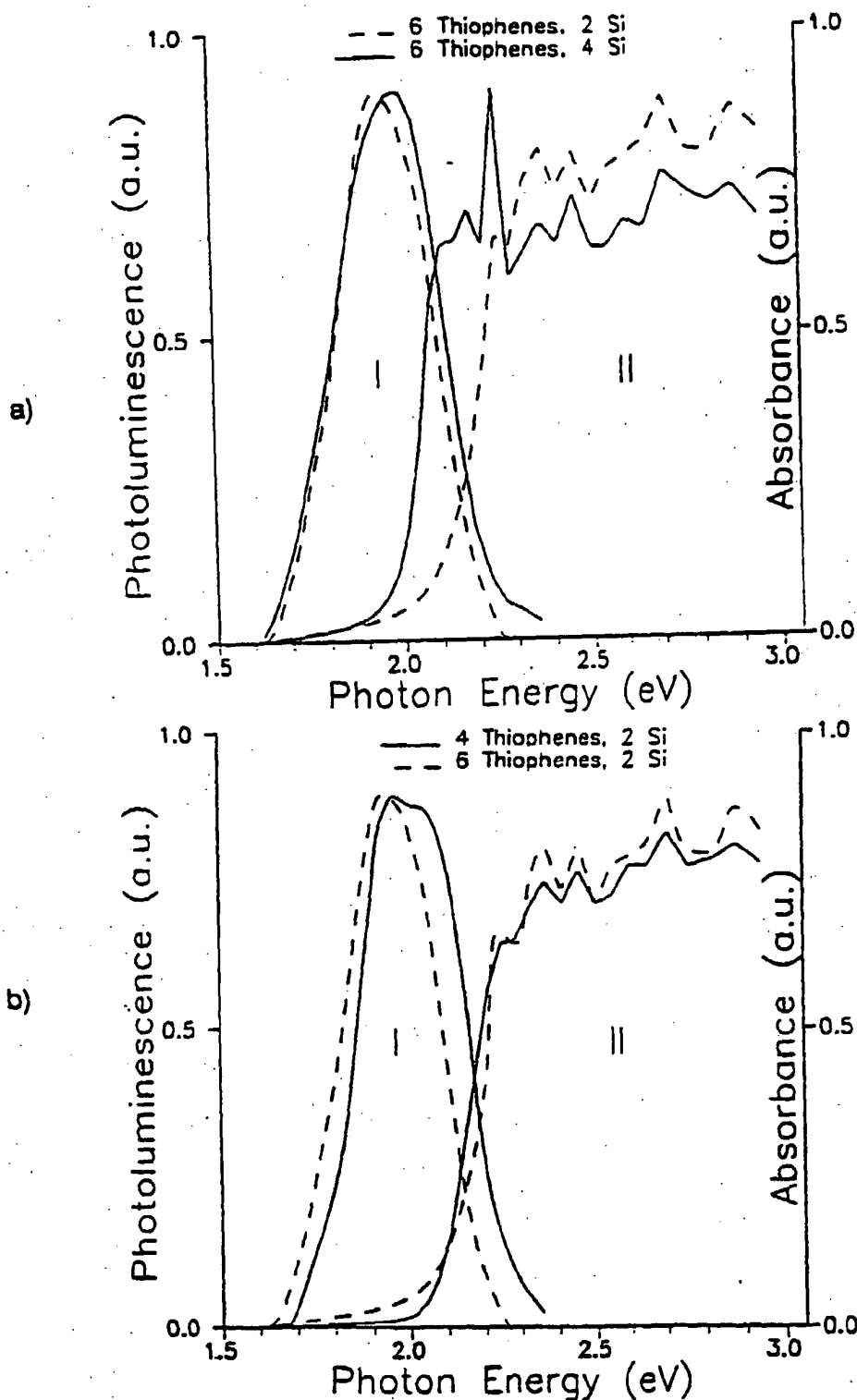
R = Alkyl, Alkoxy

B_y
($y=1-8$)



Multi-block copolymers with π and σ -conjugated blocks and conjugated/non-conjugated blocks.

FIG. 4



Preliminary spectroscopic characterization of thin films of multiblock copolymers with oligothiophenes and oligosilane blocks.

I. Photoluminescence, II. Absorption spectra.

a) By increasing the length of the oligosilane chain we observe a blue shift in the photoluminescence spectra and a red shift in the absorption spectra.

b) By increasing the length of the oligothiophene chain we observe a red shift in the photoluminescence spectrum.

FIG.5

SUBSTITUTE SHEET (P. 1 OF 2)

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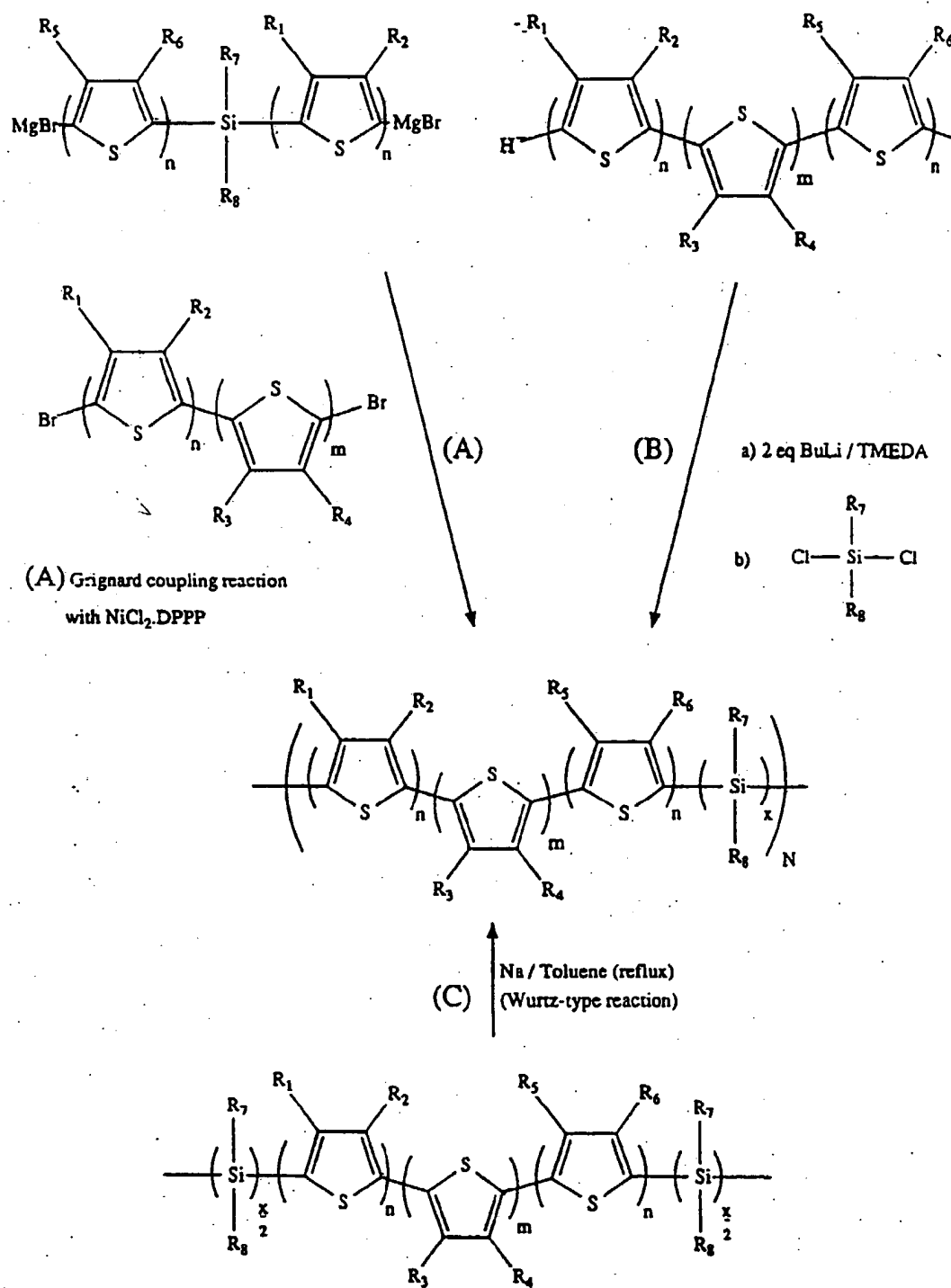


FIG. 6

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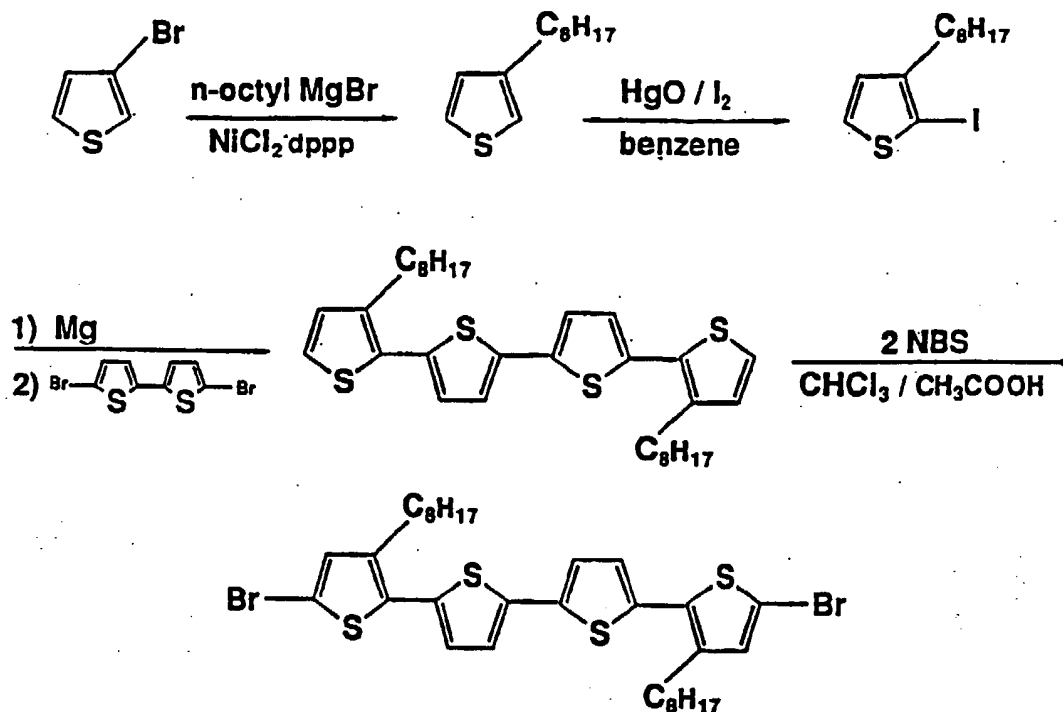


FIG. 7

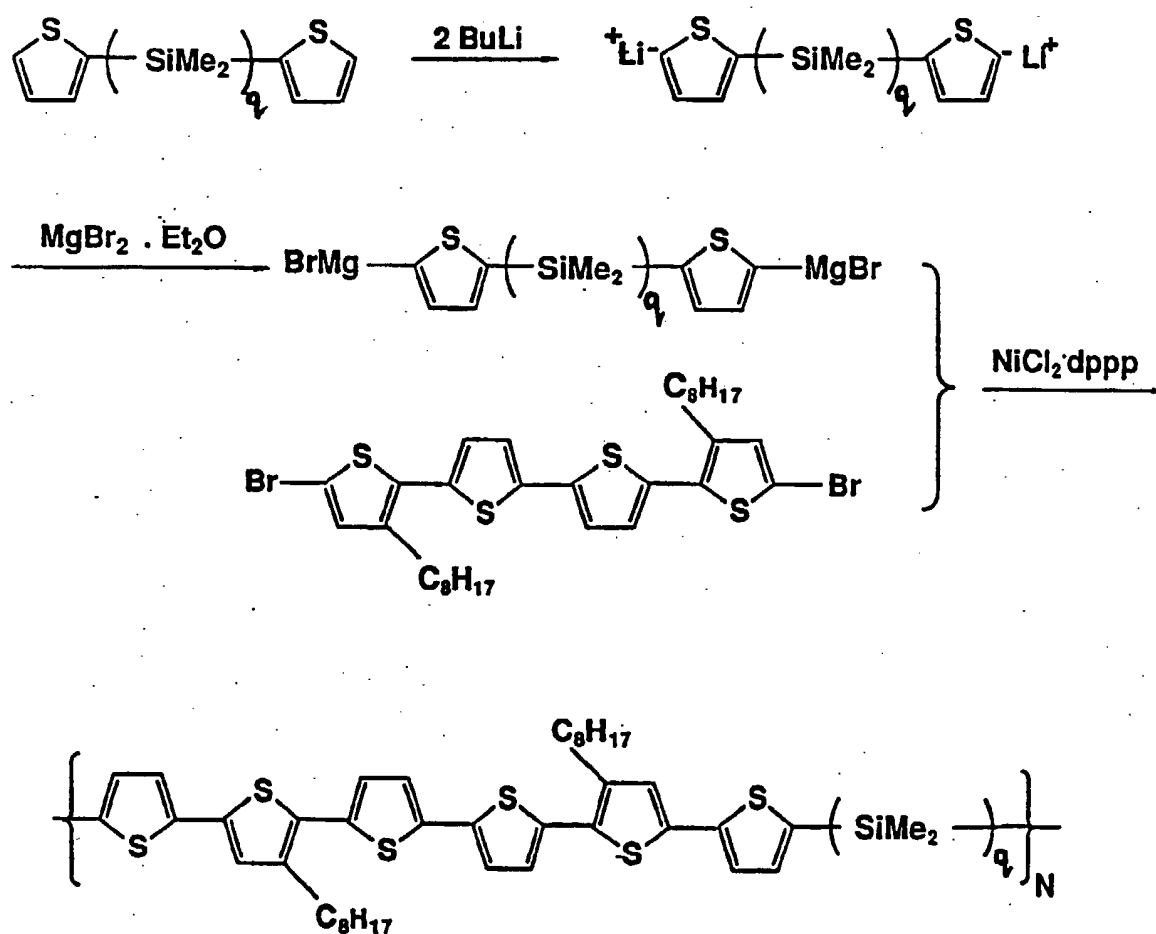


FIG. 8

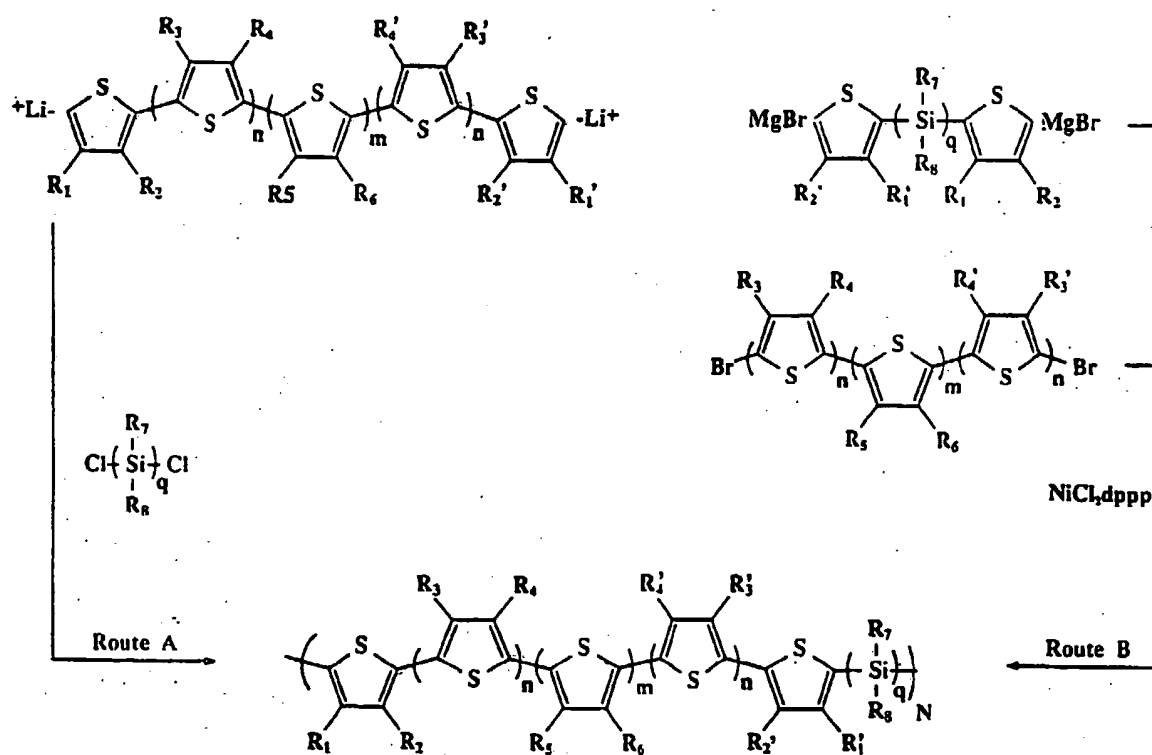


FIG. 9

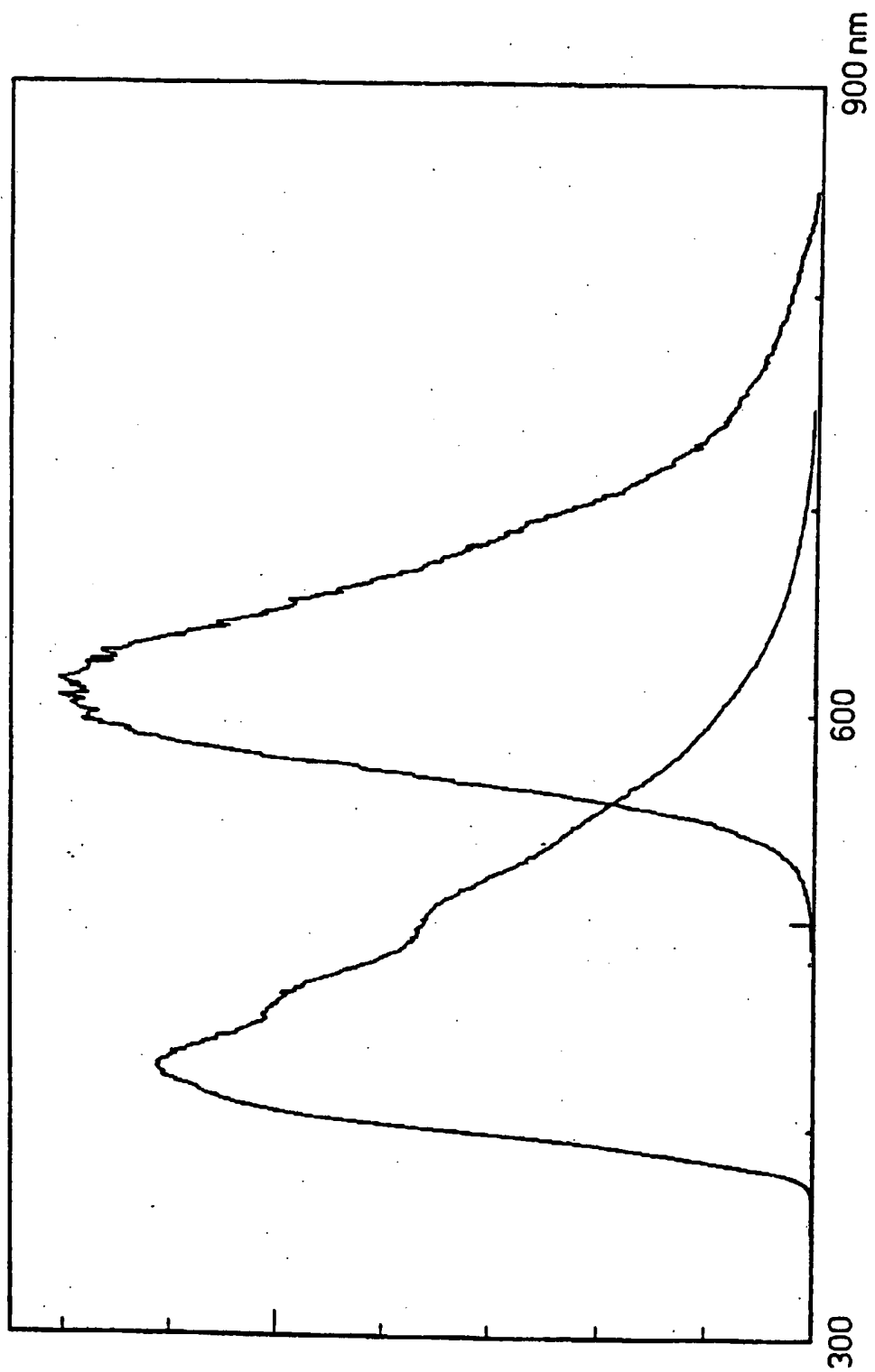


FIG.10

A. CLASSIFICATION OF SUBJECT MATTER IPC 5 H01L33/00 H05B33/14 C09K11/06 C08G77/60				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 5 H01L H05B C09K C08G G08G				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
A	NATURE vol. 356 , 5 March 1992 , LONDON GB pages 47 - 49 P.L.BURN ET AL. 'Chemical Tuning of Electroluminescent Copolymers to improve Emission Efficiencies and allow Patterning' cited in the application the whole document ---	1,2,6		
A	WO,A,92 16023 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 17 September 1992 see page 8, line 20 - page 9, line 25 claims --- -/--	1-3,9		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.				
<input checked="" type="checkbox"/> Patent family members are listed in annex.				
* Special categories of cited documents : <table border="0"> <tr> <td style="vertical-align: top;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family			
Date of the actual completion of the international search 13 May 1994		Date of mailing of the international search report 0 1. 06. 94		
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016		Authorized officer Goossens, A		

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>NATURE vol. 357, 11 June 1992, LONDON GB G. GUSTAFSSON 'Flexible Light-Emitting Diodes made from soluble conducting polymers' cited in the application the whole document</p> <p>---</p>	1,9
A	<p>FR,A,2 655 655 (RHONE - POULENC) 14 June 1991 see page 2, line 18 - line 26 see page 5, line 10 - line 32 see page 7, line 1 - line 9</p> <p>---</p>	1-4, 10-24
A	<p>MACROMOLECULES vol. 24, no. 8, 15 April 1991, WASHINGTON, DC, US pages 2106 - 2108 XP000218353 JOJI OHSITA ET AL 'Polymeric Organosilicon Systems. 10. Synthesis and Conducting Properties of Poly[2,5-(disilanylene)thienylenes]'</p> <p>-----</p>	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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WO-A-9216023	17-09-92	AU-A- 1445292	06-10-92
		EP-A- 0573549	15-12-93
FR-A-2655655	14-06-91	NONE	